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<p>(21) International Application Number: PCT/US91/04954 (22) International Filing Date: 12 July 1991 (12.07.91) (30) Priority data: 568,088 16 August 1990 (16.08.90) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: WILLIAMS, Jerry, W. ; Post Office 33427, Saint Paul, MN 55133-3427 (US). DEVOE, Robert, J. ; Post Office 33427, Saint Paul, MN 55133-3427 (US).</p> <p>X 1-3 p 35 12-29 38 13-24 39 27-40 pg 40 28</p>		<p>(74) Agents: SHERMAN, Lorraine, R. et al.; Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: POLYMERIC MIXTURES AND PROCESS THEREFOR</p> <p>(57) Abstract</p> <p>A tough polymeric mixture comprises the polymerized product of admixture I or II, wherein admixture I comprises 5 to 45 weight percent of a first monomer and a photoinitiator therefor, said first monomer being at least one free-radically polymerizable monomer, and 95 to 55 weight percent of a second monomer and a photoinitiator therefor, said second monomer being at least one set of polyurethane precursors, and admixture II comprises 5 to 45 weight percent of a first monomer and a photoinitiator therefor, said first monomer being at least one set of polyurethane precursors, and 95 to 55 weight percent of a second monomer and a photoinitiator therefor, said second monomer being at least one free-radically polymerizable monomer, said polymeric mixture having been prepared by a process involving two sequential actinic radiations of wavelength ranges centered around λ_1 and λ_2, respectively, wherein λ_1 and λ_2 differ from each other by at least 30 nm, and wherein the actinic radiation centered around λ_1 does not substantially polymerize the second monomer, and wherein the area under a stress-strain curve as determined by ASTM D638-89 for said polymeric mixture is at least 10 percent greater, preferably 20 percent greater, and more preferably at least 50 percent greater when said precursor monomers are cured by said sequential photoinitiation process compared to when the same mixture is cured by a single photostage cure.</p>		

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POLYMERIC MIXTURES AND PROCESS THEREFORField of the Invention

5 This invention relates to tough polymeric mixtures and to a process for providing tough, durable polymeric mixtures comprising a free-radically polymerized monomer in combination with a polyurethane. The polymeric mixtures are useful as vibration damping
10 materials, as protective coatings, and as tough self-supporting films.

Background of the Invention

15 Various polymeric coatings and articles are produced in processes involving use of organic solvents. Such processes require a latent catalyst or latent reaction promoter which can be activated in a controlled fashion. There is an intense effort by
20 environmentalists, researchers, law makers, and industry to promote high solids and 100% solids formulations and processes to reduce or eliminate use of such solvents and attendant costs and environmental contamination.

 WO 8802879 teaches a free-radically polymerizable composition comprising a free-radically
25 polymerizable material and a photoinitiator system comprising a free-radical photoinitiator and a ferrocenium salt. The composition may contain one or more cationically polymerizable materials. No detail is provided as to the nature of these cationically
30 polymerizable materials, nor do they teach sequential exposure to actinic radiation. Polyurethane precursors are not disclosed.

 U.S. Patent 4,849,320 teaches an imaging system containing a combination of two different
35 photoinitiators used with two different polymerizable monomers in combination with irradiation at two substantially

different wavelengths. The monomers can be acrylates and epoxies or other cationically polymerizable monomers and the photoinitiators can include ferrocenium, onium salts or an alpha cleavage or homolytic bond cleavage photoinitiator. Polyurethane precursors are not disclosed.

EPO 335,629 discloses photoresists and printing plates comprising cationically polymerizable materials (epoxy) in combination with free-radically polymerizable materials, and photoinitiators for both materials. A photopolymerization process involving exposure to varied wavelengths of radiation is also disclosed. No polyurethane precursors are taught.

EPO 344,910 discloses a photopolymerizable composition comprising a polymeric precursor, an optional photosensitizer and a two-component curing agent. The polymeric precursors are selected from ethylenically unsaturated monomers, or an ethylenically unsaturated monomer and one of epoxy and polyurethane precursors. The curing agent contains an organometallic salt and an onium salt. Similarly, EPO 344,911 discloses a polymerizable composition comprising a polymeric precursor, a curing agent containing an organometallic salt and a solvent. The polymeric precursors are selected from ethylenically-unsaturated monomers alone, and in combination with either polyurethane precursors or epoxy monomers. There is no teaching that sequential photocuring can provide a polymer mixture with superior toughness.

U.S. Patent Nos. 4,342,793 and 4,787,850 disclose compositions containing unsaturated monomers and polyurethane precursors wherein the unsaturated monomers are radiation-curable. Radiation-curing of the polyurethane precursors is not taught.

U.S. Patent No. 3,833,404 discloses a viscoelastic layer for use in a damping means for a vibratory part, the layer being an interpenetrating

polymeric network which is broadly stated to consist essentially of a polyurethane and a poly(methacrylate). There is no disclosure to a sequential photocuring process and the benefits that can be derived therefrom.

5

Summary of the Invention

Briefly, the present invention provides a tough polymeric mixture cured by a sequential photoinitiation process, wherein said polymeric mixture comprises the polymerized product of 5 to 45 weight percent of a first monomer and a photoinitiator therefor, the first monomer being one of 1) a free-radically polymerizable monomer and 2) a set of polyurethane precursors, and 95 to 55 weight percent of a second monomer and a photoinitiator therefor, the second monomer being the member of 1) and 2) that is not selected as the first monomer, and wherein the area under a stress-strain curve as determined by ASTM D638-89 for said polymeric mixture is at least 10 percent greater, preferably 20 percent greater, and more preferably at least 50 percent greater, and most preferably at least 70 percent greater when said precursor monomers are cured by said sequential photoinitiation process compared to that mixture when cured by a single photostage process.

25

In another aspect, this invention provides a process for preparing the tough polymer mixture of the invention comprising the steps:

- a) providing admixture I or II wherein

30

admixture I comprises 5 to 45 weight percent of a first monomer and a photoinitiator therefor, said first monomer being at least one free-radically polymerizable monomer, and 95 to 55 weight percent of a second monomer and a photoinitiator therefor, said second monomer being at least one set of polyurethane precursors, and

35

admixture II comprises 5 to 45 weight percent of a first monomer and a photoinitiator therefor, said first monomer being at least one set of polyurethane precursors, and 95 to 55 weight percent of a second monomer and a photoinitiator therefor, said second monomer being at least one free-radically polymerizable monomer, and

b) exposing sequentially said admixture I or II to first and second actinic radiations of wavelength ranges centered around λ_1 and λ_2 , respectively, wherein said first actinic radiation activates said photoinitiator of said first monomer without substantially activating said photoinitiator for said second monomer, and wherein said second actinic radiation activates said photoinitiator for said second monomer, and

wherein λ_1 and λ_2 differ from each other by at least 30 nm, preferably there is a difference in the range 30 to 700 nm, more preferably there is a difference in the range of 30 to 500 nm, and most preferably there is a difference in the range of 30 to 350 nm, and

wherein the first actinic radiation does not substantially polymerize the second monomer, and

wherein the area under a stress-strain curve as determined by ASTM D638-89 for said polymeric mixture is at least 10 percent greater, preferably at least 20 percent greater, and more preferably at least 50 percent greater, and most preferably at least 70 percent greater when said precursor monomers are cured by said sequential photoinitiation process compared to when cured by a single photostage curing process.

It is to be appreciated that actinic radiation generally represents a range of wavelengths known as a band width. Sequential radiations can have portions of their band widths overlapping, but λ_1 and λ_2 differ by at least 30 nm.

It has been found preferable, in order to provide a tough polymer mixture, to expose the monomer present in lesser amount to a first actinic radiation, and to expose the monomer present in greater amount to a second and subsequent actinic radiation. The two exposures are sequential in time, it being most preferred to have the second exposure immediately follow the first exposure. It may be desirable in some embodiments to subject the admixture to heat (subsequent, concurrent, or prior) to one or both of the exposures to actinic radiation.

By subjecting the polymerizable compositions of the invention to a sequential photoinitiation process via application of sufficient energy in the form of a combination of wavelengths of actinic radiation, photochemically reactive species catalyze both polyurethane formation and initiate free-radical polymerization. While certain cationic photoinitiators such as organometallic complex salts will photoinitiate both polymerizations, they are not extremely efficient free-radical photoinitiators, and it is more efficient to use a separate free-radical initiator to initiate the free-radical reaction. The process requires no drying ovens to remove solvents and provides essentially no volatile matter.

In another aspect, the present invention provides a vibration-damping constrained-layer construction which is a laminate of one or more stiff layers or substrates and one or more layers of a tough polymeric mixture according to the present invention comprising a free-radically polymerized monomer and a polyurethane to damp vibrations of component parts of a device or structure. The constrained-layer construction is affixed by mechanical or adhesive means to a solid article in need of vibration damping. These constructions comprise:

A. a stiff layer or substrate which is any web or sheet having a stiffness of at least 0.40 (relative to stainless steel) that causes it to resonate in response to an internal or external applied force, and

5 B. a layer of viscoelastic polymer which is a polymeric network derived from free-radically polymerizable monomers and urethane precursors having a storage modulus, G' , above 1×10^6 dynes per square centimeter and a loss tangent, $\tan \delta$, above 0.5,
10 preferably above 0.6, at temperatures in the range of -60 to 180°C , preferably in the range of 50 to 150°C ., and at frequencies of 20,000 Hertz or less, said layer having a thickness in the range of 0.01 to 100 mm.

15 In yet another aspect, this invention provides a protective coating on a support.

In a still further aspect, this invention provides a tough self-supporting film comprising the inventive polymerized mixture.

20 In this application:

"sequential photoinitiation process" or "sequential photocuring process" means photoinitiation of polymerization by irradiating a polymerizable mixture with actinic radiation which stimulates photochemically
25 an initiator or catalyst for one of reactive species selected from polyurethane precursors and free-radical photopolymerizable monomers, followed by irradiation of the mixture with actinic radiation to stimulate photochemically the initiator of the other reactive
30 species;

"single photostage curing" means curing monomers by one exposure to actinic radiation from a single light source;

35 "energy-induced curing" means curing by means of electromagnetic radiation (ultraviolet and visible), and thermal (infrared and heat) means or any combination thereof such as heat and light simultaneously, or in any

sequence, e.g., heat followed by light, light followed by heat followed by light, and the like;

"free-radically polymerizable monomer" means at least one monomer that polymerizes by a free-radical mechanism; the monomer can be bifunctional and includes acrylates and methacrylates, vinyl esters, vinyl aromatic compounds, etc.;

"polyurethane precursors" or a "set of polyurethane precursors" means a polymerizable mixture of one or more monomers selected from diisocyanates and polyisocyanates, and one or more monomers bearing at least two isocyanate-reactive groups. The preferred isocyanate-reactive groups are hydroxyl groups. The ratio of isocyanate groups to isocyanate-reactive groups can be from 1:2 to 2:1;

"bifunctional monomer" means a monomer that contains at least two free-radically polymerizable groups;

"bireactive monomer" means those monomers which contain both at least one free-radically polymerizable group and at least one isocyanate or isocyanate-reactive group;

"group" means a chemical species that allows for substitution or which may be substituted by conventional substituents which do not interfere with the desired product, e.g., substituents can be alkoxy, phenyl, halo (F, Cl, Br, I), cyano, nitro, etc.;

each of wavelengths " λ_1 and λ_2 " represents a useful local maximum intensity;

"actinic radiation" means electromagnetic radiation in the range of 200 to 900 nm that is capable of initiating a chemical reaction; preferably actinic radiation means visible and ultraviolet radiation;

"catalytically-effective amount" means a quantity sufficient to effect polymerization of the curable composition to a polymerized product at least to

a degree to cause an increase in the viscosity of the composition under the conditions specified;

"organometallic salt" means an ionic salt of an organometallic complex cation, wherein the cation contains at least one carbon atom of an organic group which is bonded to a metal atom of a transition metal series (Basic Inorganic Chemistry, F. A. Cotton, G. Wilkinson, Wiley: New York, 1976, p 497);

"transition metal series" means those metals in the Periodic Table Groups 4, 5, 6, 7, 8, 9, and 10 (as designated in the IUPAC system); and

"photoinitiator system" means a combination of at least one free-radical polymerization photoinitiator and at least one photocatalyst for polymerization of polyurethane precursors; and

"photoinitiator" and "photocatalyst" are used interchangeably in this application.

While not being bound by theory, it is believed that compositions comprising preferred ratios of free-radically polymerizable monomer(s), polyurethane precursors, and photoinitiator system allows formation of a multiphase material with high levels of mixing of the two polymers. Some systems will form a semi-interpenetrating polymer network (semi-IPN); some systems a true IPN. Existence of the multiphase structure provides improved toughness and may provide increased strength.

Detailed Disclosure of Preferred Embodiments of the Invention

Free-radically polymerizable monomers useful in the present invention preferably can be selected from acrylate, methacrylate, and vinyl ester functionalized materials. Of particular use are acrylate and methacrylate materials. They can be monomers and/or oligomers such as (meth)acrylates, (meth)acrylamides, N-vinylpyrrolidone and vinylazlactones as disclosed in

U.S. Patent No. 4,304,705. Such monomers include mono-, di-, or polyacrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, isooctyl acrylate, isobornyl acrylate, isobornyl methacrylate, acrylic acid, n-hexyl acrylate, tetrahydrofurfuryl acrylate, N-vinylcaprolactam, N-vinylpyrrolidone, acrylonitrile, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethylene glycol diacrylate, diethylene glycol-diacrylate, triethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 2-phenoxyethyl acrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexaacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, 2,2-bis[1-(3-acryloxy-2-hydroxy)]propoxyphenylpropane, tris(hydroxyethyl)isocyanurate trimethacrylate; the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight 200-500, copolymerizable mixtures of acrylated monomers such as those disclosed in U.S. Patent No. 4,652,274, and acrylated oligomers such as those disclosed in U.S. Patent No. 4,642,126.

Polymerizable compositions of the invention may contain ratios (weight percent) of free-radically polymerizable monomers to polyurethane precursors of 95:5 to 55:45 and 45:55 to 5:95. Preferred compositions contain ratios of from about 95:5 to 55:45. Highly preferred compositions contain ratios of from about 90:10 to about 60:40. At these highly preferred ratios, preferred polymeric mixtures of this invention exhibit superior durability and toughness properties when compared to those properties of polymeric mixtures cured by single photostage curing.

It is preferred that each polymer in the polymeric mixture be independently crosslinked. It is less preferred, but useful mixtures do result, when only the first polymerized component (which is present in lesser amount) of the mixture is crosslinked. This can be accomplished by providing in the range of 0.05 to 75 weight percent, more preferably 0.1 to 50 weight percent of each of polyurethane precursors and free-radically polymerizable monomers with polymerizable functionality greater than 2. It frequently is advantageous to use a different weight percent multifunctional monomer for each precursor. The degree of crosslinking can be varied depending on the intended application. Particularly useful as crosslinkers are polyurethane precursors such as Desmodur NTM polyisocyanates (Mobay Corp.), the biuret of isophorone diisocyanate, isocyanurates of tolylene diisocyanates, mixed isocyanurate of tolylene diisocyanate and hexamethylene diisocyanate, and reaction product of 1 mole of trimethylol propane and 3 moles of tolylene diisocyanate.

Particularly useful as crosslinkers are compounds having isocyanate reactive functionality greater than 2.05, e.g., trimethylol propane, trimethylol ethane, glycerol, 1,2,6-hexanetriol, and pentaerythritol.

Particularly useful as crosslinkers are acrylates such as allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexaacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, 2,2-bis[1-(3-acryloxy-2-hydroxy)]propoxyphenylpropane,

tris(hydroxyethyl)isocyanurate trimethacrylate; and the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight 200-500.

5 The polyurethane precursors useful in the present invention comprise an isocyanate component containing at least two isocyanate groups and an isocyanate-reactive component containing at least two isocyanate-reactive hydrogen atoms which preferably are polyols.

10 The polyisocyanate component of the polyurethane precursors may be any aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic polyisocyanate, or any combination of such polyisocyanates.

15 Particularly suitable polyisocyanates correspond to the formula



I

20 in which p is an integer 2, 3, or 4, and Q represents a di-, tri-, or tetravalent-radical aliphatic hydrocarbon containing from 2 to 100 carbon atoms and zero to 50 heteroatoms, a cycloaliphatic hydrocarbon radical containing from 4 to 100 carbon atoms and zero to 50
25 heteroatoms, an aromatic hydrocarbon radical or heterocyclic aromatic radical containing from 5 to 15 carbon atoms and zero to 10 heteroatoms, or an araliphatic hydrocarbon radical containing from 8 to 100 carbon atoms and zero to 50 heteroatoms. The heteroatoms
30 that can be present in Q include non-peroxidic oxygen, sulfur, non-amino nitrogen, halogen, silicon, and non-phosphino phosphorus.

Examples of such polyisocyanates include, but are not limited to: ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene
35 diisocyanate, trimethylhexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, 1-

isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane,
2,4- and 2,6-hexahydro-1,3-phenylene diisocyanate and
2,4-and 2,6-hexahydro-1,4-phenylene diisocyanate, and
mixtures of these isomers, perhydro-2,4'- and 4,4'-
5 diphenylmethane diisocyanate and mixtures of these
isomers, 1,3- and 1,4-phenylene diisocyanate, 2,4- and
2,6-tolylene diisocyanate and mixtures of these isomers,
2,4'- and 4,4'-diphenylmethane diisocyanate, and mixtures
of these isomers, naphthalene-1,5-diisocyanate, and the
10 reaction products of four equivalents of the above stated
isocyanate-containing compounds with compounds containing
two isocyanate-reactive groups.

It is also within the scope of the present
invention to use, e.g., triphenylmethane-4,4',4''-
15 triisocyanate, polyphenyl polymethylene polyisocyanates,
as described in G.B. Nos. 874,430, and 848,671. Also
useful are meta- and para-isocyanatophenylsulfonyl
isocyanates, perchlorinated aryl polyisocyanates,
polyisocyanates containing carbodiimide groups,
20 norbornane diisocyanates, polyisocyanates containing
allophanate groups, polyisocyanates containing
isocyanurate groups, polyisocyanates containing urethane
groups, polyisocyanates containing acrylated urea groups,
polyisocyanates containing biuret groups, polyisocyanates
25 produced by telomerization reactions of the type
described in, inter alia, U.S. Patent No. 3,654,106,
polyisocyanates containing ester groups, polyisocyanates
containing polymeric fatty acid groups, and reaction
products of any of the above-mentioned diisocyanates with
30 acetals according to German Patent No. 1,072,385, or
mixtures of any of the above polyisocyanates.

Also useful are blocked polyisocyanates, many
of which are commercially available, wherein the blocking
group can be, e.g., phenol, epsilon-caprolactam,
35 hydroxamic acid ester, ketoxime, *t*-butyl acetoacetate and
others disclosed in Wicks, Z. W., Jr. Progress in Organic
Coatings 1981, 9, 3-28.

Preferred polyisocyanates are aliphatic, such as hexamethylene diisocyanate, the isocyanurate and the biuret thereof such as Desmodur NTM from Mobay Corp., 4,4'-methylenebis(cyclohexyl isocyanate); 1-isocyanato-
5 3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate) and the biurets thereof; the tolylene diisocyanates and the isocyanurates thereof; the mixed isocyanurate of tolylene diisocyanate and hexamethylene diisocyanate; the reaction product of one mole of
10 trimethylolpropane and 3 moles of tolylene diisocyanate and crude diphenylmethane diisocyanate.

Suitable isocyanate-reactive groups contain at least two isocyanate-reactive hydrogen atoms. They can be high or low molecular weight compounds having a weight
15 average molecular weight of from about 50 to about 50,000. Useful compounds are those including amino groups, thiol groups, carboxyl groups, and hydroxyl groups.

Preferably, isocyanate-reactive compounds
20 contain hydroxyl groups, particularly compounds containing from about 2 to 50 hydroxyl groups, and more particularly, compounds having a weight average molecular weight of from about 200 to 25,000, more preferably from about 200 to 20,000, for example, polyesters, polyethers,
25 polythioethers, polyacetals, polycarbonates, poly(meth)acrylates, and polyester amides, containing at least 2, generally from about 2 to 8, but preferably from about 2 to 4 hydroxyl groups, or even hydroxyl-containing prepolymers of these compounds. Representatives of the
30 above-mentioned compounds used in accordance with the present invention are described, for example, in Saunders, J. H.; Frisch, K. C., Polyurethanes, Chemistry and Technology; High Polymers XVI; Wiley-Interscience: New York, 1962, and in Kunststoff-Handbuch;
35 Viewig-Hochtlén, R., Ed.; Carl-HanserVerlag: Munich, 1966; Vol. 1, pp 45-71. It is, of course, possible to use mixtures of the above-mentioned compounds containing

at least two hydroxyl groups and having a molecular weight of from about 50 to 50,000 for example, mixtures of polyethers and polyesters.

In some cases, it is particularly advantageous to combine
5 low-melting and high-melting polyhydroxyl containing compounds with one another (see, for example, German Offenlegungsschrift No. 2,706,297).

Low molecular weight compounds containing at least two reactive hydroxyl groups (molecular weight from
10 about 50 to 400) suitable for use in accordance with the present invention are compounds preferably containing from about 2 to 8, more preferably from about 2 to 4 reactive hydroxyl groups. It is also possible to use mixtures of different compounds containing at least two
15 hydroxyl groups and having a molecular weight in the range of from about 50 to 400. Examples of such compounds are ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4- and 2,3-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol,
20 1,4-bis(hydroxymethyl)cyclohexane, 2-methyl-1,3-propanediol, dibromobutanediol, glycerol, trimethylolpropane, 1,2,6-hexanetriol, trimethylolethane, pentaerythritol, quinitol, mannitol, sorbitol, diethylene glycol, triethylene glycol, tetraethylene glycol, higher
25 polyethylene glycols, dipropylene glycol, higher polypropylene glycols, dibutylene glycol, higher polybutylene glycols, 4,4'-dihydroxydiphenylpropane and dihydroxymethylhydroquinone.

Other polyols suitable for the purposes of the
30 present invention are the mixtures of hydroxy aldehydes and hydroxy ketones ("formose") or the polyhydric alcohols obtained therefrom by reduction ("formitol") which are formed in the autocondensation of formaldehyde, polymers thereof and hydrates thereof, in the presence of
35 metal compounds as catalysts and compounds capable of enediol formation as co-catalysts (disclosed, for example, in German Offenlegungsschrift Nos. 2,639,084;

2,714,084; 2,714,104; 2,721,186; 2,738,154; and 2,738,512).

Useful polyfunctional alcohols include poly(ethylene glycol), e.g., CarbowaxTM polyether glycols (Union Carbide), poly(propylene glycol), and
5 poly(tetramethylene glycol) such as TerathaneTM polyether glycols (Dupont).

Other useful isocyanate-reactive compounds are disclosed in Saunders, J. H.; Frisch, K. C.,
10 Polyurethanes, Chemistry and Technology; High Polymers XVI; Wiley-Interscience: New York, 1962, and Kunststoff-Handbuch; Viewig-Hochtlen, R., Ed.; Carl-HanserVerlag: Munich, 1966; Vol. 1, pp 45-71.

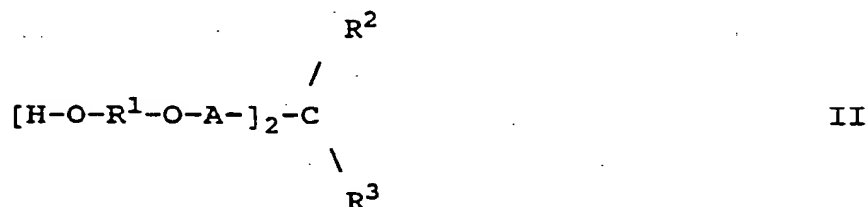
Preferred isocyanate-reactive compounds are
15 polyols having molecular weights in the range from 200 to 20,000 grams per mole, and containing two or more primary hydroxyl groups per molecule. The preferred polyols can be divided into four groups. The first three groups consist of commercially available polyols. These include
20 polyether polyols, polyester polyols, and acrylic polyols.

Preferred polyester polyols include DesmophenTM 670-80; DesmophenTM 670-100, DesmophenTM 800, and 1100, all available from Mobay Corporation. Also preferred are
25 certain polyester polyols available from Union Carbide Corp. under the trademark ToneTM, i.e., ToneTM 200, 210, 230, 240, 260, 301, 305, and 310.

Preferred polyether diols include Carbowax 400, 600, 800, 1000, 3350, 8000, and 20000, and
30 TerathaneTM 1000 and TerathaneTM 2000.

A preferred acrylic polyol is JoncrylTM 587, available from S. C. Johnson & Son, Inc. Other preferred polyols include alkyl and cycloalkyl polyols, e.g., 2,5-hexanediol, 1,6-hexanediol, ethylene glycol, DimerolTM, a
35 36 carbon essentially linear diol available from General Mills Chemicals, Inc., glycerol, 1,2,6-hexanetriol, pentaerythritol, and 1,4-cyclohexanediol.

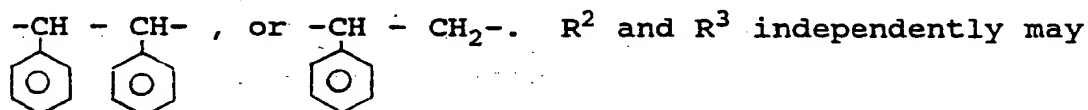
The fourth group of preferred polyols consists of hydroxyalkylated bisphenol derivatives. Preferred diols in this group have the following formula:



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where R^1 is either a straight or branched or cyclic alkylene (such as methylene, ethylene, and decylene) group consisting of 1 to 10 carbon atoms or an aralkylene group consisting of 7 to 14 carbon atoms such as benzylidene,

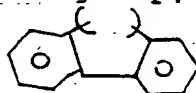
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be an alkyl group, aralkyl group, cycloalkyl group, alkaryl group, or an aryl group of 1 to 30 carbon atoms (preferably methyl, ethyl, and trifluoromethyl), and none or 1 to 10 heteroatoms, and R^2 and R^3 together can comprise an alkylene group, cycloalkylene group, arylene group, preferably

25



aralkylene group containing 2 to 660 carbon atoms, and none or 1 to 10 heteroatoms. A can be a substituted or unsubstituted arylene group, preferably having 6 to 12 carbon atoms, most preferably *p*-phenylene, *o*-phenylene, and dimethylnaphthylene.

30

Specific preferred hydroxyalkylated bisphenols are 9,9-bis-4-(2-hydroxyethoxyphenyl)fluorene (hydroxyethylated bisphenol of fluorenone), 2,2-bis-4-(2-hydroxyethoxyphenyl)butane (hydroxyethylated bisphenol of butanone), 2,2-bis-4-(2-hydroxyethoxyphenyl)hexafluoropropane (hydroxyethylated bisphenol F), and

35

1,2-bis-4-(2-hydroxyethoxyphenyl)propane,
2,2-bis-4-(2-hydroxyethoxyphenyl)norbornane,
2,2-bis-4-(2-hydroxyethoxyphenyl)-5,6-cyclopentanorbornane
and 1,1-bis-4-(2-hydroxyethoxyphenyl)cyclohexane.

5

Another group of monomers which are useful in compositions of the invention are bireactive monomers which serve as crosslinkers, i.e., those that possess at least one free-radically polymerizable group and one isocyanate or isocyanate-reactive functionality. Such monomers include, for example, 2-isocyanatoethyl methacrylate, 3-isopropenophenyl isocyanate, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and hydroxybutyl acrylate. Bireactive monomers comprise up to 25 mole percent of the isocyanate or isocyanate-reactive groups, preferably they comprise less than 5 mole percent of the isocyanate or isocyanate reactive groups, and up to 50 mole percent of free-radically polymerizable monomers, preferably less than 25 mole percent of free-radically polymerizable monomers. Most preferably, the compositions are free of bireactive monomers.

Urethane photocatalysts include electron withdrawing group-substituted diazonium salts as described in U.S. Patent No. 4,544,466, and salts of organometallic complex cations such as are disclosed in U.S. Patent No. 4,740,577. The preferred class of initiators are organometallic complex salts which are disclosed in detail in U.S. Patent No. 4,740,577, col. 3, line 39, to col. 12, line 40.

M, the metal atom in the cationic portion of the organometallic salt, can be any transition metal from Periodic Groups 4, 5, 6, 7, 8, 9, and 10 (IUPAC system) such as, for example, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt. In the preferred compositions, M is Co, Fe, Mn, Re, Mo or Cr. In the most preferred compositions, M is Fe.

Illustrative of preferred anions are
 $B(\text{phenyl})_4^-$, $B(\text{phenyl})_3(\text{alkyl})^-$, where alkyl can be ethyl,
 propyl, butyl, hexyl and the like, BF_4^- , PF_6^- , AsF_6^- ,
 SbF_6^- , $FeCl_4^-$, $SnCl_5^-$, SbF_5^- , AlF_6^- , $GaCl_4^-$, InF_4^- , TiF_6^- ,
 5 ZrF_6^- , and sulfonates such as $CF_3SO_3^-$, $C_8F_{17}SO_3^-$,
 p-toluenesulfonate, and p-chlorobenzenesulfonate, etc.
 More preferably, the anions are BF_4^- , PF_6^- , SbF_6^- ,
 SbF_5OH^- , AsF_6^- , and $SbCl_6^-$.

Preferred salts of organometallic complex
 10 cations useful in the compositions of the invention are
 those having the formula $[(L^5)(L^6)M]^{+e}X_f$, where L^5 is
 selected from the class of substituted and unsubstituted
 aromatic compounds based on a benzene or cyclopentadienyl
 nucleus, L^6 which optionally is present can be a group
 15 donating an even number of sigma electrons (such as CO,
 NO^+ , substituted or unsubstituted phosphines,
 phosphites), M is Fe, e is 1 or 2 and X_f is
 tetrafluoroborate, hexafluorophosphate,
 hexafluoroarsenate or hexafluoroantimonate.

20 Examples of preferred salts of organometallic
 complex cations useful in the composition of the
 invention include the following:

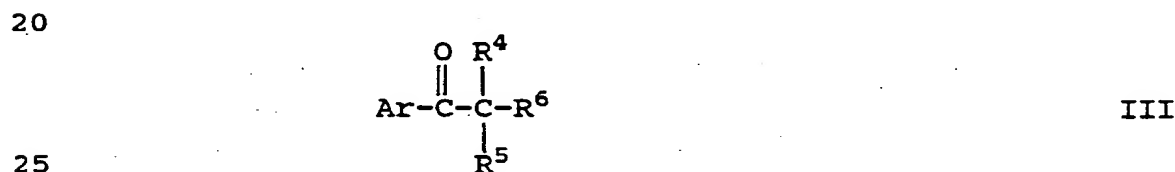
(η^6 -benzene)(η^5 -cyclopentadienyl)iron(1+)
 hexafluoroantimonate
 25 (η^6 -toluene)(η^5 -cyclopentadienyl)iron(1+)
 hexafluorophosphate
 (η^6 -cumene)(η^5 -cyclopentadienyl)iron(1+)
 hexafluorophosphate
 30 (η^6 -p-xylene)(η^5 -cyclopentadienyl)iron(1+)
 hexafluorophosphate
 (η^6 -o-xylene)(η^5 -cyclopentadienyl)iron(1+)
 hexafluorophosphate
 (η^6 -m-xylene)(η^5 -cyclopentadienyl)iron(1+)
 35 hexafluorophosphate

- (η^6 -mesitylene)(η^5 -cyclopentadienyl)iron(1+)
hexafluorophosphate
- (η^6 -hexamethylbenzene)(η^5 -
5 cyclopentadienyl)iron(1+) hexafluoroantimonate
(η^6 -naphthalene)(η^5 -
cyclopentadienyl)iron(1+) hexafluoroantimonate
(η^6 -pyrene)(η^5 -cyclopentadienyl)iron(1+)
- 10 hexafluoroantimonate
(η^6 -perylene)(η^5 -cyclopentadienyl)iron(1+)
hexafluoroantimonate
(η^6 -chrysene)(η^5 -cyclopentadienyl)iron(1+)
hexafluoroantimonate
- 15 (η^6 -acetophenone)(η^5 -
methylcyclopentadienyl)iron(1+) hexafluoroantimonate
(η^6 -fluorene)(η^5 -cyclopentadienyl)iron(1+)
hexafluoroantimonate
bis(η^6 -mesitylene)iron(2+)
- 20 hexafluoroantimonate.
Electron withdrawing group substituted
diazonium salts useful as urethane photocatalysts are
those disclosed in U.S. Patent No. 4,544,466 and include
- 25 p-chlorobenzenediazonium tetrafluoroborate,
p-chlorobenzenediazonium hexafluorophosphate,
p-bromobenzenediazonium hexafluorophosphate,
p-fluorobenzenediazonium hexafluorophosphate,
p-iodobenzenediazonium hexafluoroarsenate,
p-nitrobenzenediazonium hexafluoroarsenate,
- 30 p-nitrobenzenediazonium tetrafluoroborate,
2,4-dichlorobenzenediazonium tetrafluoroborate,
2,4-dibromobenzenediazonium hexafluoroarsenate,
2,4-dichlorobenzenediazonium hexafluorophosphate,
2,4-dichlorobenzenediazonium pentafluorostannate,
- 35 2,4-dichlorobenzenediazonium hexafluorobismuthate,
2,4,6-trichlorobenzenediazonium tetrafluoroborate,
2,4,6-trichlorobenzenediazonium hexafluorophosphate,

2,4,6-trichlorobenzenediazonium hexafluoroarsenate,
 2,4,6-trichlorobenzenediazonium hexafluoroantimonate,
 2,4-dinitrobenzenediazonium pentafluorostannate,
 2,6-dichlorobenzenediazonium hexafluoroborate, and
 5 mixtures thereof.

The free-radical photoinitiator can be selected from those compounds that generate free-radicals upon exposure to actinic radiation, e.g., those compounds disclosed in Vesley, G. F., J. Radiat. Curing 1986,
 10 January, 4, and U.S. Patent No. 4,747,432. Photoinitiators are selected from acetophenones and ketals, benzophenones, aryl glyoxalates, acylphosphine oxides, sulfonium and iodonium salts, diazonium salts and peroxides. Preferred additional free-radical initiators
 15 that are light activated are those that have an absorption maximum in the 300 to 400 nm region of the electromagnetic spectrum.

Especially useful are acetophenones and ketals corresponding to the formula:



wherein Ar is a C₆-C₁₄ aryl group which is unsubstituted or substituted by halogen, CN, OH, or groups such as
 30 C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, phenoxy, C₁-C₁₂ thioalkyl, SCH₂CH₂OH, thiophenyl, C₁-C₁₂ SO₂alkyl, SO₂phenyl, C₂-C₁₃ COOalkyl, SO₂NH₂, C₁ to C₁₂ SO₂NHalkyl, C₂ to C₂₄ SO₂N(alkyl)₂, C₁-C₁₂ NHalkyl, C₂-C₂₄ N(alkyl)₂, C₂-C₁₃ NHCOalkyl or NHCO-phenyl, or represents thienyl, pyridyl,
 35 furyl, indanyl or tetrahydronaphthyl, and preferably alkyl represents a lower alkyl radical of 1 to 4 carbon atoms;

R⁴ can be OH, a C₁-C₈ alkyl group which is unsubstituted or substituted by -OH, alkoxy, C₂-C₈acyloxy,
 40 -COOalkyl or CN, or is C₂-C₄alkenyl, C₅-C₆cycloalkyl,

C₇-C₉phenylalkyl, or -OR⁷ wherein R⁷ is C₁-C₈alkyl which is unsubstituted or substituted by -OH, alkoxy, C₂-C₈acyloxy, -COOalkyl, -CN or phenyl, or C₆aryl; and

5 R⁵ has one of the meanings assigned to R⁴, a C₂-C₈ alkenylene group or together with R⁴ represents a C₂-C₈ cycloalkylene group or a C₃-C₉ oxacycloalkylene group or azacycloalkylene group; and

10 R⁶ is hydrogen, OH, C₁-C₈alkyl group, C₆-C₁₄aryl group, C₅-C₈ cycloalkyl group or morpholino group.

Such compounds have been disclosed, for example, in U.S. Patent Nos. 3,715,293, 3,728,377, 4,284,485 and 4,318,791, all of which are incorporated herein by reference for these compounds.

15 Preferred compounds have R⁴ and R⁵ independently chosen from -OR⁸, wherein R⁸ can be C₁-C₄ alkyl group and R⁶ can be a phenyl group; or R⁴ and R⁵ combining to form C₂-C₈ cycloalkylene group, preferably cyclohexylene group, and R⁶ can be -OH or phenyl group.

20 Typical alkyl groups in R⁴, R⁵ and R⁶ include methyl, ethyl, propyl, isobutyl, t-butyl, pentyl, neopentyl, hexyl, heptyl, octyl, 2-ethylhexyl; aryl groups include phenyl, naphthyl, anthracyl, tolyl, xylyl, methoxyphenyl, halophenyl, hydroxyphenyl, nitrophenyl and 25 carboethoxyphenyl; and cycloalkyl groups include cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, ethylcyclopentyl, cyclohexyl, methylcyclohexyl, cycloheptyl, bicycloheptyl, cyclooctyl, and bicyclooctyl.

30 Illustrative acetophenones include:

2,2-dimethoxyacetophenone
2,2-dimethoxy-2-phenylacetophenone
2,2-diethoxyacetophenone
2,2-dibutoxyacetophenone
35 2,2-dihexyloxyacetophenone
2,2-di(2-ethylhexyloxy)acetophenone
2,2-diphenoxyacetophenone

- 2,2-ditolylloxyacetophenone
2,2-di(chlorophenyl)acetophenone
2,2-di(nitrophenyl)acetophenone
2,2-diphenoxy-2-phenylacetophenone
5 2,2-dimethoxy-2-methylacetophenone
2,2-dipropoxy-2-hexylacetophenone
2,2-diphenoxy-2-ethylacetophenone
2,2-dimethoxy-2-cyclopentylacetophenone
2,2-di(2-ethylhexyl)-2-cyclopentylacetophenone
10 2,2-diphenoxy-2-cyclopentylacetophenone
2,2-di(nitrophenoxy)-2-cyclohexylacetophenone
2,2-dimethyl-2-hydroxyacetophenone
2,2-diethoxy-2-phenylacetophenone
2,2-diphenethyloxy-2-phenylacetophenone
15 2,2-(2-butenediylloxy)-2-phenylacetophenone
2,2-dimethyl-2-morpholino-(p-thiomethyl)
acetophenone
1-hydroxycyclohexyl phenyl ketone.

Also preferred are aromatic onium salts as
20 free-radical photoinitiators. These salts are disclosed,
for example in U.S. Patent Nos. 4,069,054, 4,231,951 and
4,250,203. Such salts are described by the formula

AW

IV

25

wherein A is an organic cation selected from
those described in U.S. Patent Nos. 3,708,296, 3,729,313,
3,741,769, 3,794,576, 3,808,006, 4,026,705, 4,058,401,
4,069,055, 4,101,513, 4,216,288, 4,394,403, and
30 4,623,676, which are incorporated herein by reference,
preferably selected from diazonium, iodonium, and
sulfonium cations, more preferably A is selected from
diphenyliodonium, triphenylsulfonium and phenylthiophenyl
diphenylsulfonium; and W is an anion where W preferably
35 can be CF_3SO_3^- , BF_4^- , PF_6^- , SbF_6^- , SbF_5OH^- , AsF_6^- , and
 SbCl_6^- .

Photoinitiators which are useful for partially polymerizing alkyl acrylate monomers without crosslinking, to prepare a partially polymerized syrup, discussed below, include the benzoin ethers (such as benzoin methyl ether or benzoin isopropyl ether), substituted benzoin ethers (such as anisoin methyl ether), substituted acetophenones (such as 2,2-diethoxyacetophenone and 2,2-dimethoxy-2-phenylacetophenone), substituted alpha-ketols (such as 2-methyl-2-hydroxypropiophenone), aromatic sulfonyl chlorides (such as 2-naphthalenesulfonyl chloride) and photoactive oximes. Photoinitiators may be used for syrup-making in amounts which, when dissolved, are present in an amount of about 0.001 to 0.5 percent by weight of the alkyl acrylate monomer, preferably at least 0.01 percent.

A suitable photoinitiator system which includes organometallic complex ionic salts described above and a free-radical initiator contains those combinations that, upon application of two exposures of actinic radiation of λ_1 and λ_2 as defined above, provide a polymeric mixture having superior toughness. Preferably, each of λ_1 and λ_2 are in the range of 250 to 800 nm and preferably in the range of 300 to 600 nm of the electromagnetic spectrum, with the proviso that λ_1 and λ_2 differ from each other by at least 30 nm, preferably there is a difference in the range 30 to 700 nm, more preferably there is a difference in the range of 30 to 500 nm, and most preferably there is a difference in the range of 30 to 350 nm. Most preferably λ_1 is greater than λ_2 . The level of catalytic activity depends on various factors such as the choice of metal, ligands, and counterions in the organometallic salt and selection of the free-radical photoinitiator.

By sequentially exposing the polymerizable compositions of this invention to actinic radiation according to the prescribed method described above, the

polymeric precursor which is the minor component of the mixture (present in an amount in the range of 5 to 45 weight percent) is polymerized first without substantially polymerizing the major component. By "not substantially polymerizing" is meant that the polymerization of a component has occurred to an extent such that the gel point for that component has not been reached. Extent of conversion at the gel point can be calculated using the Flory-Stockmayer equation (Odiان, G., Principles of Polymerization, 2nd Ed.; Wiley: New York, 1981; pp 112-119, equation 2-165):

for polyurethane precursors,

$$P_c = 1/\{r[1-\rho_{NCO}(f_{NCO} - 2)][1 + \rho_{OH}(f_{OH} - 2)]\}^{1/2}$$

for free radically polymerizable monomers,

$$P_c = 1/[1 + \rho_x(f_x - 2)]$$

wherein

P_c is the fractional conversion of monomer to polymer at the gel point,

r is a ratio, always less than one, of the lesser of isocyanate reactive groups and isocyanate groups to the greater of isocyanate reactive groups and isocyanate groups,

ρ_{NCO} is the fraction of isocyanate groups belonging to isocyanate compounds bearing greater than two isocyanate groups,

ρ_{OH} is the fraction of isocyanate reactive groups belonging to compounds bearing greater than two isocyanate reactive groups,

ρ_x is the fraction of free radically polymerizable groups belonging to compounds bearing greater than one free radically polymerizable group,

f_{NCO} , f_{OH} , and f_x are the average functionality of compounds bearing greater than two isocyanate groups, greater than two isocyanate reactive groups, and greater than one free radically polymerizable group, respectively, wherein the functionality of each isocyanate group and each isocyanate reactive group is one, and the functionality of each free radically polymerizable group is two.

The sequential photoinitiation method as disclosed herein is particularly useful when the polyurethane precursor is not compatible with or soluble in the free-radically polymerizable monomer at room temperature. The process allows for heating the precursors to a temperature which will allow achieving compatibility or solubility without prematurely initiating cure. Subsequent sequential exposures to actinic radiation provide the desired cure.

In general, the photoinitiator system should be present in a catalytically effective amount. Typically, the photoinitiator system can be present in the range of 0.01 to 20, preferably 0.02 to 5 weight percent of the total polymerizable composition. The ratio of the organometallic complex salt (or other polyurethane initiator) to free-radical initiator is generally in the range of 1:100 by weight to 100:1 by weight. Preferably, the weight ratio is in the range of 1:10 and 10:1.

Energy polymerizable compositions of this invention are radiation-sensitive and additionally they can be polymerized in a two stage polymerization process wherein one or both radiations can be followed by heat. Heat can also be applied before or during the irradiation process to promote polymerization of the composition.

When desired, photosensitizers may be incorporated into the photopolymerizable compositions. Use of photosensitizers alters the wavelength sensitivity of radiation-sensitive compositions employing the latent

photocatalysts and photoinitiators of this invention. This is particularly advantageous when the latent photocatalyst or photoinitiator does not strongly absorb the incident radiation. Use of a photosensitizer
5 increases the radiation sensitivity, allowing shorter exposure times and/or use of less powerful sources of radiation. When cationic organometallic salts are used, any photosensitizer may be useful if its triplet energy is at least 45 kilocalories per mole. Examples of such
10 photosensitizers are given in Table 2-1 of Murov, S. L., Handbook of Photochemistry; Marcel Dekker: New York, 1973; pp 27-35, and include pyrene, fluoranthrene, xanthone, thioxanthone, benzophenone, acetophenone, benzil, chrysene, p-terphenyl, acenaphthene, naphthalene,
15 phenanthrene, biphenyl, substituted derivatives of the preceding compounds, and the like. When present, the amount of photosensitizer used in the practice of the present invention is generally in the range of 0.01 to 10 parts, and preferably 0.1 to 1.0 part, by weight, of
20 photosensitizer per part of organometallic salt.

Long wavelength sensitizers may be added, i.e., dyes. Suitable sensitizers are believed to include compounds in the following categories of dyes: ketones, aminoketones, coumarins (e.g., ketocoumarins), xanthenes,
25 acridines, thiazoles, thiazines, oxazines, azines, porphyrins, aromatic polycyclic hydrocarbons, aminotriaryl methanes, merocyanines, and squarylium and pyridinium salts.

Other useful materials which can be blended
30 into compositions of the invention include, but are not limited to, adjuvants such as fillers, pigments, fibers, woven and nonwoven fabrics, foaming agents, antioxidants, stabilizers, fire retardants, free-radical inhibitors, and viscosity adjusting agents.

35 Where divided, the steps are preferably arranged in the following order. The first step is to mix the free-radically photopolymerizable monomer(s)

containing a single polymerizable group with an effective amount of a free-radical initiator. Any bireactive monomers desired can be added during any step except that isocyanate-containing bireactive monomers preferably are added in the fourth step described infra. Preferably, this free-radical initiator does not also function as a crosslinking agent. The second step is to irradiate the composition, and allow it to polymerize so that the viscosity is increased. This will provide a partially polymerized syrup typically having a Brookfield viscosity of 300 to 20,000 centipoise at room temperature, preferably, from 500 to 2000 centipoise. The increased viscosity provides a syrup that is a more suitable coating composition. If a photoinitiator is used for this process, the partial polymerization may be stopped at any point simply by turning off the irradiation source. Alternatively, the syrup can be prepared by conventional thermal polymerization techniques and then quenched with air to attain the desired viscosity. Alternatively, the organometallic photoinitiator may be mixed with an alkyl acrylate monomer and then partially polymerized to form a syrup. The syrup can also be mixed with a viscosity adjusting agent, such as a hydrophilic silica to obtain a suitable viscosity for coating.

25 The third step is to mix the isocyanate reactive component into the syrup created in steps two and three.

 The fourth step is to mix the syrup with isocyanate component.

30 The organometallic photoinitiator, crosslinking agent, and an additional amount of free-radical initiator may be added at any time after the step two irradiation. The photoinitiators may be mixed with any component. The finished modified syrup may be coated onto a backing and exposed to energy to complete the polymerization.

35

Alternatively, the composition may be made by mixing all monomers except the isocyanate with an effective amount of a free-radical initiator, partially polymerizing to increase viscosity, then adding the organometallic complex salt, crosslinking agent, additional free-radical photoinitiator, and the isocyanate, and following up by a sequential photoinitiation process.

In still an additional method, step one can be omitted, and all monomers and crosslinking agent can be mixed with a free radical photoinitiator and an organometallic photoinitiator, and following up by a sequential photoinitiation process.

Temperature of polymerization and amount of catalyst will vary depending on the particular photopolymerizable composition used and the desired application of the polymerized product. The amount of the total photoinitiator system to be used in this invention should be a catalytically-effective amount under the desired use conditions. As previously stated, such amount generally will be in the range of about 0.01 to 20 weight percent, and preferably 0.02 to 5 weight percent, based on the weight of curable composition.

Solvents, preferably organic, can be used to assist in dissolving of the photoinitiator system in the free-radically polymerizable monomers and polyurethane precursors and as a processing aid. It may be advantageous to prepare a concentrated solution of the organometallic complex salt in a solvent to simplify the preparation of the photopolymerizable composition. Representative solvents include organic solvents such as propylene carbonate, acetone, methyl ethyl ketone, cyclopentanone, methyl cellosolve acetate, methylene chloride, nitromethane, methyl formate, acetonitrile, gamma-butyrolactone, and 1,2-dimethoxyethane (glyme). In some applications, it may be advantageous to adsorb the

photoinitiator onto an inert support such as silica, alumina, clays, etc., as described in U.S. Patent No. 4,677,137, incorporated herein by reference.

Compositions containing an organometallic complex salt and a free-radical photoinitiator may be photopolymerized by exposure to any source of radiation, particularly radiation sources emitting radiation in the ultraviolet and visible region of the spectrum (e.g., about 200 to 800 nm). Suitable sources of radiation include mercury vapor discharge lamps, carbon arcs, tungsten lamps, xenon lamps, lasers, sunlight, and the like. The required amount of exposure to effect polymerization is dependent upon such factors as the identity and concentrations of the organometallic complex salt and free-radical photoinitiator; the specific free-radically polymerizable monomers and the polyurethane precursors, thickness of the exposed material which can be e.g., 0.04 mm to 25 cm, intensity of the radiation source and amount of heat associated with the radiation.

For the multiple photoinitiation process, light centered around two different wavelengths is employed in combination with a set of (at least two) photoinitiators. These photoinitiators frequently have absorption maxima at differing wavelengths. In such case, use of actinic radiation having substantially different wavelengths will generally be required. This increased control over the order of polymerization provides a consonant increase in the ability to control the final properties of the composition. Such radiation can be provided in a number of ways. Different radiation sources of substantially different wavelengths can be used. The wavelengths of major intensity for each source can be obtained from examination of the spectral output of each source. One source could be used for different wavelength regions through use of filters or monochromators. Lasers or other monochromatic light

sources are also useful. For example, a tungsten lamp, whose output is mainly in the visible region, could be used as one light source while a lamp whose output is concentrated around 360 nm, e.g., a black light, could be
5 used as another source.

Thermal means using direct heating or infrared electromagnetic radiation, as it is known in the art, can be used to aid in polymerizing the free-radically polymerizable monomers and the polyurethane precursors
10 according to the teachings of this invention. It is also possible to use microwave irradiation to provide thermal energy to aid in polymerizing the compositions of this invention.

It is within the scope of this invention to
15 use multiple wavelengths of actinic radiation by irradiating the photopolymerizable compositions sequentially. In the preferred method, photopolymerization is effected by sequential exposure to a radiation source emitting active radiation in the
20 visible region of the spectrum, followed by exposure to a radiation source in the ultraviolet region of the spectrum. It is also preferred to heat either during or after irradiation in the visible region. In addition, it may be desirable to subsequently thermally polymerize the
25 activated precursor so obtained, the irradiation temperatures being below the temperature employed for subsequent heat postcuring. These activated precursors may normally be polymerized at temperatures which are substantially lower than those required for direct
30 thermal polymerization, with an advantage in the range from 50°C to 110°C. This process also makes it possible to control polymerization in a particularly simple and advantageous manner.

In the current state of the art, free-radical
35 photopolymerization preferably is carried out in an inert atmosphere. Any inert atmosphere such as nitrogen, carbon dioxide, helium or argon is suitable. A

sufficiently inert atmosphere can be achieved by covering a layer of the photoactive mixture with a plastic film which is transparent to ultraviolet radiation and irradiating through that film in air. The composition
5 should be kept in low light, or preferably total darkness, in air, vacuum, or inert gaseous atmosphere until ready for photopolymerization.

The present invention composition has utility
10 as a vibration damping material. Properties of vibration-damping materials are described in the literature. Nielsen, L.E., Mechanical Properties of Polymers, Van Nostrand Reinhold: New York, 1965; pp 162-165, discloses that materials possessing the
15 maximum vibration-damping capability have shear storage moduli, G' , greater than 10^7 dynes/cm² but less than 10^{10} dynes/cm² at the use temperature. Furthermore, Rosen, S.L., Functional Principles of Polymeric Materials for Practicing Engineers; Barnes and Noble: New York, 1971;
20 pp 222-227, shows that it is desirable for a vibration-damping material to have both a storage modulus and a loss tangent with values as high as possible.

Yerges, L.F., Sound, Noise, and Vibration Control; Van Nostrand Reinhold: New York, 1965; pp 68-69,
25 notes that useful damping materials exhibit decay rates from as low as 5 to 80 dB/sec (decibels/second), and from 1/2 to 20 percent of critical damping. ("Critical" damping is the damping necessary to just prevent oscillation).

Damping materials are applied to structures
30 and component parts in devices to attenuate resonant vibrations and thereby reduce noise and vibrational fatigue. This is often accomplished by attaching a viscoelastic material of appropriate damping
35 characteristics to the vibrating structure. The vibrational forces cause the viscoelastic material to undergo deformation where some of its inelastic

deformation energy is converted to heat and then dissipated (mechanical hysteresis). Under cyclic loading, the heat generated results in a temperature rise until the heat generated per cycle is equal to the heat dissipated through conduction, convection and radiation. Thus, the ability of a material to damp is measured by its ability to convert vibrational energy to heat energy.

In viscoelastic materials, the maximum amount of energy is dissipated as heat at the glass-rubber transition temperature. The effectiveness of a viscoelastic material in energy dissipation is evaluated by measuring its viscoelastic response to a periodic stress or strain. Results of the dynamic mechanical test are generally given in terms of the storage modulus, E' or G' , and the loss modulus, E'' or G'' . E is Young's modulus and G is the shear modulus. E'' (or G'') is the damping or energy dissipation term. The angle which reflects the time lag between the applied strain and stress is known as δ , and is defined by the ratio called the dissipation factor or loss factor. $\tan(\delta)$ is a damping term and is a measure of the ratio of energy dissipated as heat to the maximum energy stored in the material during one cycle of oscillation; $\tan(\delta) = G''/G'$ (or E''/E').

As is known in the art, the most efficient use of the damping material occurs if the material is sandwiched between the panel to be damped and a relatively stiff layer, such as a thin metal sheet. This forces the damping material into shear as the panel vibrates, dissipating substantially more energy than when the material acts simply in extension and compression.

Solid articles comprising the viscoelastic polymeric mixtures of the invention are prepared by either of two processes. In a first process, a layer of the polymerizable mixture is coated onto a release liner, the mixture polymerized, and the layer of resulting polymeric mixtures transferred to a substrate and adhered

thereto, thereby providing a constrained-layer construction. In the second process, a layer of the polymerizable mixture is coated directly onto a substrate and the mixture polymerized in situ thereby also
5 providing a constrained-layer construction. The constrained-layer construction is then mechanically (e.g., as by bolting) or adhesively affixed to the solid article that requires vibration damping. When the solid article subsequently vibrates under the influence of an
10 internal or external applied force, vibration in the solid article is damped.

Since the viscoelastic polymer often has adhesive properties, the polymer can usually be adhered to a stiff layer or substrate without the use of an
15 adhesive. It is sometimes desirable, however, to use a thin layer (e.g., 20-50 μm) of high-modulus adhesive, such as an acrylic adhesive or an epoxy adhesive, to bond the polymer to a solid article which can be, for example, an oil pan, a valve cover, or a transmission housing.

20 For most applications, the layer of viscoelastic polymer is a coating having a thickness of at least 0.01 mm up to about 100 mm, preferably 0.025 to 100 mm, and most preferably 0.05 to 100 mm. The coating can be applied by any of the techniques known in the art
25 such as by spray, dip, knife, or curtain coating.

As mentioned above, a stiff layer or substrate is an essential part of the constrained-layer vibration-damping constructions of the present invention.

A suitable material for a substrate has a stiffness of
30 at least 0.40 (relative to stainless steel) as defined in Handbook of Tables for Applied Engineering Science, Bolz, R.E. et al., eds., CRC Press: Cleveland, Ohio, 1974, p 130. The desired stiffness of the substrate is varied by adjusting the thickness of the layer, for example from
35 about 25 micrometers to 5 centimeters, depending on the modulus of the substrate. Examples of suitable materials include metals such as iron, steel, nickel, aluminum,

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chromium, cobalt and copper, and alloys thereof and stiff polymeric materials such as polystyrene, polyvinylchloride, polyurethane, polycarbonate, and polyepoxide, glass fiber-reinforced plastics such as glass fiber, ceramic fiber, and metal fiber-reinforced polyester, glasses, and ceramics. The process for polymerization of the composition may be completed in one step, or may be divided into several steps separated by an interval of time, where such is preferable.

10 The tough polymeric mixtures of the invention provide impact resistant protective coatings on a variety of substrates, such as glass, metal, wood, ceramics, paper, and polymers. The coating can be stripped from a support bearing a release layer to provide a self-supported film. Release layers are well-known in the art.

20 Objects and advantages of this invention are further illustrated by the following examples, but they should not be construed as limiting the invention; the scope of which is defined by the claims.

Example 1

25 In a glass jar was placed 80 parts of isooctyl acrylate mixed with 20 parts of N-vinylpyrrolidone. 85 parts of this mixture was mixed with 0.04 parts Irgacure™ 651 (free radical initiator (2,2-dimethoxy-2-phenylacetophenone, Ciba-Geigy Corp., Ardsley, NY). The mixture was continuously stirred using a magnetic stirrer and deoxygenated by bubbling nitrogen gas through the solution for at least 5 minutes. The mixture was then exposed to radiation from two Blacklight™ blue lamps (Sylvania, Eagan, MN, no. F15T8/BLD) for about 45 seconds resulting in about 10% acrylate conversion corresponding to a viscosity of about 1500 centipoise (Prepolymer A).

35 To this prepolymer was added 15 parts of hydroxyethylated bisphenol of fluorenone. The mixture was then heated on a water bath to about 80-90°C to

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dissolve the diol. An additional 0.1 part of IrgacureTM 651 was added along with 0.03 part of inorganic photocatalyst,
(eta⁶-xylene)(eta⁵-cyclopentadienyl)iron(1+)
5 hexafluorophosphate, 0.1 part of hexanediol diacrylate, and 12.33 parts of an isocyanate mixture containing a 1:1 weight ratio of DesmodurTM N100 (Mobay Corp., Pittsburgh, PA) and isophorone diisocyanate. The jar was capped and shaken to achieve thorough mixing. The hot mixture was
10 then degassed under vacuum to remove air bubbles and dissolved oxygen.

The mixture was coated using a knife edge coater. The coater was heated with infrared lamps just prior to coating. The mixture was coated between two
15 liners of 15.2 cm (6 inch) wide polyester films. The films were coated with a release liner to allow the cured adhesive to be removed. The coater was divided into three zones. Zone 1 consisted of four 300 watt flood lamps. Two lamps were suspended over the web and two
20 lamps were placed under the web. The lamps were placed about 5.1 cm (two inches) from the web. Zone 2 consisted of a UV irradiation zone. UV exposure was 600 mJ/cm² as measured by an EIT Light Bug (Electronic Instrumentation and Technology, Inc., Sterling, VA). The web speed was
25 45 cm (1.5 feet) per minute. The sample was post-cured in Zone 3 for 30 minutes at 100°C followed by 30 minutes at 125°C to provide a tough film. The film was easily removed from the liners to provide a self-supporting tough film.

30

Comparative Example A

Comparative Example A was formulated and processed exactly as Example 1 and processed using UV light only in a single photostage cure. The sample was
35 not exposed to radiation from the visible lamps. Toughness, modulus, and tensile data are given in TABLE 1, below.

36

Example 2

To 85 parts Prepolymer A prepared as in Example 1 was added 15 parts DesmophenTM 670-80 polyester polyol (Mobay Corp., Pittsburgh, PA). The mixture was then heated on a water bath to about 80-90°C to dissolve the polyol, then allowed to cool. An additional 0.1 parts IrgacureTM 651 was added along with 0.03 parts (eta⁶- xylene)(eta⁵-cyclopentadienyl)iron(1+) hexafluorophosphate, 0.1 parts of hexanediol diacrylate and 1.42 parts of an isocyanate mixture containing a 1:1 weight ratio of DesmodurTM N100 and isophorone diisocyanate. The jar was capped and shaken to achieve thorough mixing. The mixture was then degassed under vacuum to remove air bubbles and dissolved oxygen.

The mixture was coated and irradiated as in Example 1. The sample was post cured in Zone 3 for 30 minutes at 100°C to provide a self-supporting tough film.

Comparative Example B

Comparative Example B was formulated and processed exactly as Example 2. The processing utilized UV light only in a single photostage cure. Toughness, modulus, and tensile strength data is given in TABLE 1, below. The sample was not exposed to radiation from the visible lamps.

Examples 1 and 2 and Comparative Examples A and B were evaluated for toughness, Young's modulus and tensile strength according to ASTM standard D 638-89 using an InstronTM model 1122 testing machine. Specimens were prepared using a type IV die as discussed in ASTM D 638-89. The crosshead speed was 508 mm/min. "Toughness" is defined as the energy required to break a test specimen, and was derived from stress-strain curves by computing the area under (i.e., integration of) the curve. All toughness values are given for specimens with a cross sectional area of 6.4 mm².

37

<u>TABLE 1</u>			
Example number	Toughness (N-mm)	Young's modulus (MPa)	Tensile strength (MPa)
1	76200	1.81	5.14
A (comparative)	62100	1.41	4.55
2	656	0.039	0.63
B (comparative)	386	0.036	0.42

Data of TABLE 1 show that films cured by the sequential photoinitiation process of the invention have superior toughness, modulus, and tensile strength compared to identical formulations cured by a conventional single photostage curing process. Sample 1 shows greater than 20% improvement in toughness compared to A and Sample 2 shows greater than 50% improvement (i.e., 70%) in toughness compared to B.

The following five examples (this includes 2 comparative examples) demonstrate the general utility of the invention to produce vibration damping materials as self-supporting members. A series of coatable compositions were prepared using the following procedure.

Example 3

In glass jar were mixed 65 parts isooctyl acrylate and 35 parts N-vinylpyrrolidone. 50 parts of this mixture was mixed with 0.02 parts Irgacure™ 651. The mixture was continuously stirred using a magnetic stirrer and deoxygenated by bubbling nitrogen gas through the solution for at least 5 minutes. The mixture was then exposed to radiation from two Blacklight™ blue lamps for about 45 seconds. The reaction was allowed to go to about 10% acrylate

conversion. This corresponded to a viscosity of about 1500 centipoise. To this prepolymer was added 7.5 parts of hydroxyethylated bisphenol of fluorenone. An additional 0.05 parts of IrgacureTM 651 was added along with 0.03 parts (eta⁶-xylene)(eta⁵-cyclopentadienyl)-iron(1+) hexafluorophosphate, and 0.05 parts hexanediol diacrylate. To this mixture was added 5.42 parts of an isocyanate mixture containing a 1:1 weight ratio of DesmodurTM N100 and isophorone diisocyanate. The jar was capped and shaken to achieve thorough mixing. The mixture was then degassed under vacuum to remove air bubbles and dissolved oxygen.

The mixture was coated and irradiated as described in Example 1, then post-cured for 45 minutes at 100°C followed by 15 minutes at 125°C. The cured composition was removed from the liners.

Example 4

Another sample was prepared according to the procedure described in Example 3, except that 4.02 parts of an isocyanate mixture containing a 1:99 weight ratio of DesmodurTM N100 and isophorone diisocyanate was substituted for the 5.42 parts mixture of DesmodurTM N 100 and isophorone diisocyanate in the formulation.

Example 5

Prepolymerization was carried out in a glass jar; 35 parts of isooctylacrylate, 35 parts of isobornyl acrylate, 35 parts of N-vinylpyrrolidone were mixed with 0.04 parts of free radical initiator, IrgacureTM 651. The mixture was continuously stirred using a magnetic stirrer and deoxygenated by bubbling nitrogen gas through the solution for at least 5 minutes. The mixture was then exposed to radiation from two BlacklightTM blue lamps for about 45 seconds resulting in about 10% acrylate conversion corresponding to a viscosity of about 1500 centipoise. To this prepolymer

was added 50 parts of hydroxyethylated bisphenol of fluorenone. The mixture was then heated on a water bath to about 80°C to dissolve the diol. An additional 0.1 part of IrgacureTM 651 was added along with 0.17 part of an inorganic photocatalyst, (eta⁶-xylene)(eta⁵-cyclopentadienyl)iron(1+) hexafluorophosphate, 0.1 parts of hexanediol diacrylate and 18.07 parts of an isocyanate mixture containing a 1:1 weight ratio of DesmodurTM N100 and isophorone diisocyanate. The jar was capped and shaken to achieve thorough mixing. The mixture was then degassed under vacuum to remove air bubbles and dissolved oxygen.

The mixture was coated and irradiated as in Example 1. Subsequently, it was post-cured for 45 minutes at 100°C followed by 15 minutes at 125°C, and then removed from the liners.

Comparative Example C

Comparative Example C was the exact same formula as Example 3. The processing conditions were the same as Example 3 except that the sample was not irradiated in Zone 1 (no visible light exposure). This sample was exposed to UV irradiation only in Zone 2 (single photostage cure).

Comparative Example D

Comparative Example D was the exact same formula as Example 4. The processing conditions were the same as Example 4 except that the sample was not irradiated in Zone 1 (no visible light exposure). This sample was exposed to UV irradiation only in Zone 2 (single photostage cure).

Examples 3, 4, and 5 displayed good damping characteristics as determined by dynamic mechanical analysis on a Rheometrics Solids Analyzer RSA II (Rheometrics, Inc., Piscataway, NJ. These materials exhibited a Young's storage modulus (E') of about 1 X

10^{10} dynes/cm² in the glassy region and about 10^7 dynes/cm² in the rubbery plateau as determined from a dynamic tensile test performed at 1 Hertz. These values translated to a shear storage modulus (G') of about 3.8×10^9 dynes/cm² in the glassy regime and 3.8×10^6 dynes/cm² in the rubbery plateau via the well known relationship of $E = 2(1+\nu)G$ where ν is Poisson's ratio which varies between 0 and 0.5. Since ν is generally between 0.3 and 0.35 for plastics, $E = 2.65G$ is a good approximation.

Damping behavior as delineated via $\tan(\delta)$ was determined from dynamic mechanical experiments performed using a shear sandwich geometry and a test frequency of 1 Hertz. The temperature range for damping (useful damping materials have a $\tan(\delta) \geq 0.6$) was from about 43°C to about 140°C for Examples 3 to 5. Peak maximum of $\tan(\delta)$, the temperature at which $\tan(\delta)$ is a maximum, and the temperature interval at $\tan(\delta) \geq 0.6$ and are shown in Table 2. Examples of the invention exhibit good damping characteristics, and are suitable as the viscoelastic component in both free-layer and constrained-layer damping constructions.

TABLE 2

Example	$\tan(\delta)$ amplitude (maximum)	Temp interval at $\tan(\delta) \geq 0.6$ (°C)
3	0.89	73 (maximum at 100)
C (comparative)	0.95	31 (maximum at 48)
4	1.04	31 (maximum at 55.5)
D (comparative)	1.00	28 (maximum at 64)
5	1.36	42 (maximum at 110)

5 Data of TABLE 2 show that samples of the invention (Examples 3, 4, 5) provide a wider temperature range for good damping properties than comparative sample prepared using a single photostage curing process.

Examples 6 to 10

10 Data of the following examples are given in TABLE 4 and show utility of the invention to produce tough, impact resistant protective coatings.

15 Tetrahydrofurfuryl acrylate (SR285) (Sartomer Company, West Chester, PA) was mixed with tetraethyleneglycol diacrylate, (SR268) (Sartomer Company) in various ratios as shown in Table 3. Acrylate mixture (80 parts) was combined with 10.9 parts
20 DesmophenTM 670-100 and 3.8 parts of an isocyanate mixture containing a 1:1 weight ratio of DesmodurTM N-100 and isophorone diisocyanate. IrgacureTM 651 (0.05 parts) was added along with 0.025 part of organometallic photocatalyst,
(eta⁶-xylene)(eta⁵-cyclopentadienyl)iron(1+) hexafluorophosphate.

25 The solutions were coated on aluminum panels using a #10 wire wound bar (R.D. Specialties, Webster, NY). The coated panels were then exposed to irradiation from flood lamps placed above and below the panel. The web speed was 30 cm (1 foot) per minute. The panels were then placed in an oven at 70°C for 5 minutes. The panels were then put through three passes in a UV
30 processor (RPC Equipment UV Processor, Model QC 1202TM, PPG Industries, Plainfield, IL, under nitrogen atmosphere at 15 m/min. (50 ft/minute). The UV exposure was 1.8 joules/cm². The coated panels were then post-cured in an oven for 1 hour at 100°C prior to
35 testing.

The coated samples were tested for gloss and reverse impact strength. Gloss was measured using a

Gardner #4525 Gloss Meter (BYK Gardner, Silver Spring, MD). High gloss measurements are desirable in coatings. Gloss is correlated with smooth surfaces and clarity of coating. Reverse impact tests were performed according to ASTM standard D3029-84. The impact tests employed measure impact resistance or toughness. Crosshatch adhesion tests (to aluminum panels) was measured according to ASTM standard D 3359-78. Data are shown in TABLES 3 and 4.

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<u>TABLE 3</u> Acrylate Solution Composition (Parts by Weight)		
Example Number	SR285	SR268
6 & E	29	71
7 & F	43	57
8 & G	57	43
9 & H	71	29
10 & I	86	14

TABLE 4

Example number	Gloss % at 20°	Gloss % at 60°	Impact (N-m) at 60°	Impact (N-m) at 23°	Cross-hatch adhesion
6	99.5	100+	108	108	3
E	97.6	100+	81	14	0
7	100+	100+	135	95	3
F	7.0	15.4	81	68	2
8	100+	100+	189	122	5
G	3.4	6.5	122	135	3
9	100+	100+	203+	203+	5
H	2.2	4.5	149	162	5
10	100+	100+	203+	203+	5
I	2.0	4.3	203+	203+	5

The data of TABLE 4 show that the samples of the invention have higher gloss in all cases (aesthetic appeal for protective coatings) while maintaining equal or greater impact resistance and cross-hatch adhesion to aluminum compared to the same compositions cured in a single photostage process.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this

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invention is not to be unduly limited to the
illustrative embodiments set forth herein.

CLAIMS:

1. A tough polymeric mixture comprising the polymerized product of admixture I or II, wherein
- 5 admixture I comprises 5 to 45 weight percent of a first monomer and a photoinitiator therefor, said first monomer being at least one free-radically polymerizable monomer, and 95 to 55 weight percent of a second monomer and a photoinitiator
- 10 therefor, said second monomer being at least one set of polyurethane precursors, optionally at least one photosensitizer, and optionally at least one crosslinking agent in an amount sufficient to crosslink said first monomer or both of said monomers, and
- 15 admixture II comprises 5 to 45 weight percent of a first monomer and a photoinitiator therefor, said first monomer being at least one set of polyurethane precursors, and 95 to 55 weight percent of a second monomer and a photoinitiator therefor, said
- 20 second monomer being at least one free-radically polymerizable monomer, optionally at least one photosensitizer, and optionally at least one crosslinking agent in an amount sufficient to crosslink said first monomer or both of said monomers,
- 25 said polymeric mixture having been prepared by a process involving two sequential actinic radiations of wavelength ranges centered around λ_1 and λ_2 , respectively, wherein λ_1 and λ_2 differ from each other by at least 30 nm, and
- 30 wherein the actinic radiation centered around λ_1 does not substantially polymerize the second monomer, and
- 35 wherein the area under a stress-strain curve as determined by ASTM D638-89 for said polymeric mixture is at least 10 percent greater when said precursor monomers are cured by said sequential

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photoinitiation process compared to that mixture when cured by a single photostage curing process.

2. The polymeric mixture according to claim
5 1 wherein said free-radically polymerizable monomer is selected from the group consisting of acrylate, methacrylate, and vinyl ester functionalized materials, and wherein said polyurethane precursors comprise an isocyanate component containing at least two isocyanate
10 groups and an isocyanate-reactive component containing at least two isocyanate-reactive hydrogen atoms.

3. The polymeric mixture according to claims
15 1 and 2 wherein said photoinitiator for said polyurethane precursors is selected from the group consisting of diazonium salts and salts of transition metal-containing organometallic complex cations, and wherein said free-radical photoinitiator is selected from the group consisting of acetophenones, ketals,
20 benzophenones, benzoin ethers, triazines, arylglyoxalates, acylphosphine oxides, sulfonium salts, iodonium salts, diazonium salts, and peroxides.

4. The polymeric mixture according to claims
25 1 to 3 wherein said total photoinitiator system is present in the range of 0.01 to 20 weight percent of the total polymerizable composition.

5. The polymeric mixture according to claims
30 1 to 4 wherein the polymeric product of said first monomer is crosslinked or said polymeric product of both of said monomers is crosslinked.

6. A process for preparing a tough polymeric
35 mixture comprising the steps of:

a) providing admixture I or II according to claims 1 to 5, and

b) exposing sequentially said admixture I or II to first and second actinic radiations of wavelength ranges centered around λ_1 and λ_2 , respectively, wherein said first actinic radiation activates said
5 photoinitiator of said first monomer without substantially activating said photoinitiator for said second monomer, and wherein said second actinic radiation activates said photoinitiator for said second monomer, and

10 wherein λ_1 and λ_2 differ from each other by at least 30 nm, and

wherein the actinic radiation centered around λ_1 does not substantially polymerize the second monomer, and

15 wherein the area under a stress-strain curve as determined by ASTM D638-89 for said polymeric mixture is at least 10 percent greater when said precursor monomers are cured by said sequential photoinitiation process compared to that mixture when
20 cured by a single photostage curing process.

7. The method according to claim 6 wherein at least one of λ_1 and λ_2 is in the visible region or in the ultraviolet region of the spectrum.

25 8. The method according to claims 6 and 7 wherein at least one of said actinic radiation exposures is preceded by, is simultaneous with, or is followed by heating the mixture.

30 9. The method according to claims 6 to 8 wherein said first monomer is precured sufficiently to provide a coatable syrup.

35 10. A vibration damping material comprising a) at least one substrate, and

b) coated on at least one surface of said substrate the polymeric mixture according to claims 1 to 5.

- 5 11. A protective coating or a self-supporting film comprising the polymeric mixture according to claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/04954

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁵ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 F 2/50, C 08 G 18/10, 18/67, C 09 D 175/04																	
II. FIELDS SEARCHED <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 25%; border: 1px solid black; padding: 5px;">Classification System</td> <td style="border: 1px solid black; padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="border: 1px solid black; padding: 5px; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: 1px solid black; padding: 5px; height: 40px; vertical-align: bottom;">C 08 F; C 08 G; C 09 D</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 08 F; C 08 G; C 09 D											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category *</th> <th style="width: 70%; padding: 5px;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%; padding: 5px;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A2, 0228854 (INTEREZ, INC.) 15 July 1987, see the whole document --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A1, 0242513 (BASF LACKE + FARBEN AKTIENGESSELLSCHAFT) 28 October 1987, see the whole document --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A1, 0272346 (E.I. DU PONT DE NEMOURS AND COMPANY) 29 June 1988, see the whole document --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A2, 0344910 (MINNESOTA MINING AND MANUFACTURING COMPANY) 6 December 1989, see the whole document --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-11</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	EP, A2, 0228854 (INTEREZ, INC.) 15 July 1987, see the whole document --	1-11	A	EP, A1, 0242513 (BASF LACKE + FARBEN AKTIENGESSELLSCHAFT) 28 October 1987, see the whole document --	1-11	A	EP, A1, 0272346 (E.I. DU PONT DE NEMOURS AND COMPANY) 29 June 1988, see the whole document --	1-11	A	EP, A2, 0344910 (MINNESOTA MINING AND MANUFACTURING COMPANY) 6 December 1989, see the whole document --	1-11
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search 2nd January 1992</td> <td style="width: 50%; border: 1px solid black; padding: 5px;">Date of Mailing of this International Search Report 13. 01. 92</td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">International Searching Authority EUROPEAN PATENT OFFICE</td> <td style="border: 1px solid black; padding: 5px;">Signature of Authorized Officer <div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px 5px; margin-right: 10px;">M. PERIS</div> <div style="font-family: cursive; font-size: 1.2em;">M. Peris</div> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search 2nd January 1992	Date of Mailing of this International Search Report 13. 01. 92	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer <div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px 5px; margin-right: 10px;">M. PERIS</div> <div style="font-family: cursive; font-size: 1.2em;">M. Peris</div> </div>											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	EP, A2, 0344911 (MINNESOTA MINING AND MANUFACTURING COMPANY) 6 December 1989, see the whole document ---	1-11
A	US, A, 4342793 (SKINNER ET AL) 3 August 1982, see the whole document -- -----	1-11

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 2/50, C08G 18/10, 18/67 C09D 175/04	A1	(11) International Publication Number: WO 92/03483 (43) International Publication Date: 5 March 1992 (05.03.92)
(21) International Application Number: PCT/US91/04954 (22) International Filing Date: 12 July 1991 (12.07.91) (30) Priority data: 568,088 16 August 1990 (16.08.90) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: WILLIAMS, Jerry, W. ; Post Office 33427, Saint Paul, MN 55133-3427 (US). DEVOE, Robert, J. ; Post Office 33427, Saint Paul, MN 55133-3427 (US).		(74) Agents: SHERMAN, Lorraine, R. et al.; Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>With amended claims.</i> Date of publication of the amended claims: 16 April 1992 (16.04.92)
(54) Title: POLYMERIC MIXTURES AND PROCESS THEREFOR		
(57) Abstract A tough polymeric mixture comprises the polymerized product of admixture I or II, wherein admixture I comprises 5 to 45 weight percent of a first monomer and a photoinitiator therefor, said first monomer being at least one free-radically polymerizable monomer, and 95 to 55 weight percent of a second monomer and a photoinitiator therefor, said second monomer being at least one set of polyurethane precursors, and admixture II comprises 5 to 45 weight percent of a first monomer and a photoinitiator therefor, said first monomer being at least one set of polyurethane precursors, and 95 to 55 weight percent of a second monomer and a photoinitiator therefor, said second monomer being at least one free-radically polymerizable monomer, said polymeric mixture having been prepared by a process involving two sequential actinic radiations of wavelength ranges centered around λ_1 and λ_2 , respectively, wherein λ_1 and λ_2 differ from each other by at least 30 nm, and wherein the actinic radiation centered around λ_1 does not substantially polymerize the second monomer, and wherein the area under a stress-strain curve as determined by ASTM D638-89 for said polymeric mixture is at least 10 percent greater, preferably 20 percent greater, and more preferably at least 50 percent greater when said precursor monomers are cured by said sequential photoinitiation process compared to when the same mixture is cured by a single photostage cure.		

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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

AMENDED CLAIMS

[received by the International Bureau on 4 March 1992 (04.03.92);
original claim 1 amended; remaining claims unchanged (2 pages)]

1. A tough polymeric mixture comprising the
5 polymerized product of admixture I or II, wherein
admixture I comprises 5 to 45 weight percent
of a first monomer and a photoinitiator therefor, said
first monomer being at least one free-radically
polymerizable monomer, and 95 to 55 weight percent of a
10 second monomer and a photoinitiator therefor, said second
monomer being at least one set of polyurethane
precursors, optionally at least one photosensitizer, and
optionally at least one crosslinking agent in an amount
sufficient to crosslink said first monomer or both of
15 said monomers, and
admixture II comprises 5 to 45 weight percent
of a first monomer and a photoinitiator therefor, said
first monomer being at least one set of polyurethane
precursors, and 95 to 55 weight percent of a second
20 monomer and a photoinitiator therefor, said second
monomer being at least one free-radically polymerizable
monomer, optionally at least one photosensitizer, and
optionally at least one crosslinking agent in an amount
sufficient to crosslink said first monomer or both of
25 said monomers,
said polymeric mixture having been prepared by
a process involving two sequential actinic radiations of
wavelength ranges centered around λ_1 and λ_2 , respectively,
wherein λ_1 and λ_2 differ from each other by at least
30 30 nm, and
wherein the monomer present in lesser amount
is exposed to said first actinic radiation centered
around λ_1 and wherein said monomer present in greater
amount is exposed to said second and subsequent actinic
35 radiation centered around λ_2 ,

wherein the actinic radiation centered around λ_1 does not substantially polymerize the second monomer, and

5 wherein the area under a stress-strain curve as determined by ASTM D638-89 for said polymeric mixture is at least 10 percent greater when said precursor monomers are cured by said sequential photoinitiation process compared to that mixture when cured by a single photostage curing process.

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